

1 Constant Temperature (Tuckerman)

Our treatment of the canonical ensemble naturally raises the question of how molecular dynamics simulations can be performed under the external conditions of this ensemble. After all, as noted in the previous chapter, simply integrating Hamilton's equations of motion generates a microcanonical ensemble as a consequence of the conservation of the total Hamiltonian. By contrast, in a canonical ensemble, energy is not conserved but fluctuates so as to generate the Boltzmann distribution $\exp[-\beta\mathcal{H}]$ due to exchange of energy between the system and the thermal reservoir to which it is coupled. Although we argued that these energy fluctuations vanish in the thermodynamic limit, most simulations are performed far enough from this limit that the fluctuations cannot be neglected. In order to generate these fluctuations in a molecular dynamics simulation, we need to mimic the effect of the thermal reservoir. Various methods to achieve this have been proposed (Andersen, 1980; Nosé and Klein, 1983; Berendsen et al., 1984; Nosé, 1984; Evans and Morriss, 1984; Hoover, 1985; Martyna et al., 1992; Liu and Tuckerman, 2000). We will discuss several of these approaches in the remainder of this chapter. It must be mentioned at the outset, however, that most canonical "dynamics" methods do not actually yield any kind of realistic dynamics for a system coupled to a thermal bath. Rather, the trajectories generated by these schemes comprise a set of microstates consistent with the canonical distribution. In other words, they produce a sampling of the canonical phase space distribution from which equilibrium observables can be computed.

The most straightforward approach to kinetic control is a simple periodic rescaling of the velocities such that the instantaneous kinetic energy corresponds to a desired temperature. While easy to implement, this approach does not guarantee that a canonical phase space distribution is obtained. We can improve upon this approach by replacing

the velocity scaling by a periodic resampling of the velocities from the Maxwell- Boltzmann distribution. Such a scheme only guarantees that a canonical momentum-space distribution is obtained. Nevertheless, it can be useful in the initial stages of a molecular dynamics calculation as a means of relaxing unfavorable contacts arising from poorly chosen initial positions.

Of all the canonical dynamics methods, by far the most popular are the "extended phase space" approaches (Andersen, 1980; Nosé and Klein, 1983; Nosé, 1984; Hoover, Canonical ensemble 1985; Martyna et al., 1992; Liu and Tuckerman, 2000). These techniques supplement the physical phase space with additional variables that serve to mimic the effect of a heat bath within a continuous, deterministic dynamical scheme. The extended phase space methodology allows the greatest amount of flexibility and creativity in devising canonical dynamics algorithms. Moreover, the idea of extending the phase space has led to other important algorithmic advances such as the Car-Parrinello molecular dynamics approach (Car and Parrinello, 1985) for marrying electronic structure with finite temperature dynamics as well as methods for computing free energies (see Chapter 8).

1.1 Berendsen Thermostat

Just for historical reason, let's describe the Berendsen thermostat. It is based on the equation for the evolution of the temperature

$$\frac{dT}{dt} = \frac{T_{thermostat} - T}{\tau}$$

e.g. an exponential relaxation of the T toward the desired $T_{thermostat}$ value. Discretising the equation one obtains

$$T(t+\Delta T) = T(t) + \Delta t \frac{T_{thermostat} - T(t)}{\tau} = T(t) \left(1 + \frac{\Delta t}{\tau} \left[\frac{T_{thermostat}}{T(t)} - 1 \right] \right)$$

To achieve this time dependence, the velocities at each MD step are rescaled by a factor α

$$\alpha = \sqrt{\left(1 + \frac{\Delta t}{\tau} \left[\frac{T_{thermostat}}{T(t)} - 1 \right]\right)}$$

This thermostat does not produce the correct canonical sampling of phase space and should never be used during a production run. Can be conveniently implemented for equilibrating the system at the desired T .

1.2 Anderson Thermostat (Frenkel-Smith)

In the constant-temperature method proposed by Andersen the system is coupled to a heat bath that imposes the desired temperature. The coupling to a heat bath is represented by stochastic impulsive forces that act occasionally on randomly selected particles. These stochastic collisions with the heat bath can be considered as Monte Carlo moves that transport the system from one constant-energy shell to another. Between stochastic collisions, the system evolves at constant energy according to the normal Newtonian laws of motion. The stochastic collisions ensure that all accessible constant-energy shells are visited according to their Boltzmann weight. Before starting such a constant-temperature simulation, we should first select the strength of the coupling to the heat bath. This coupling strength is determined by the frequency of stochastic collisions. Let us denote this frequency by ν . If successive collisions are uncorrelated, then the distribution of time intervals between two successive stochastic collisions, $P(t; \nu)$, is of the Poisson form

$$P(t; \nu) = \nu e^{-\nu t}$$

Indeed, the probability of not colliding up to time t and collide in

the following dt is

$$P(t, \nu)dt = \lim_{\Delta t \rightarrow 0} (1 - \nu\Delta t)^{t/\Delta t} \nu dt =$$

and calling $t/\Delta t = n$

$$P(t, \nu) = \lim_{\Delta n \rightarrow \infty} \left(1 - \frac{\nu t}{n}\right)^n \nu = \nu e^{-\nu t}$$

A constant-temperature simulation now consists of the following steps:

- 1. Start with an initial set of positions and momenta and integrate the equations of motion for a time Δt .
- 2. A number of particles are selected to undergo a collision with the heat bath. The probability that a particle is selected in a time step of length Δt is $\nu\Delta t$.
- 3. If particle i has been selected to undergo a collision, its new velocity will be drawn from a Maxwell-Boltzmann distribution corresponding to the desired temperature T . All other particles are unaffected by this collision.

The mixing of Newtonian dynamics with stochastic collisions turns the Molecular Dynamics simulation into a Markov process. It has been shown that a canonical distribution in phase space is invariant under repeated application of the Andersen algorithm. Combined with the fact that the Markov chain is also irreducible and aperiodic, this implies that the Andersen algorithm does, indeed, generate a canonical distribution.

```
subroutine integrate(switch, f,en,temp)
if (switch.eq.1) then
  do i=1,npart
    x(i) =x(i) +dt*v(i) + dt*dt*f(i)/2
```

```

    v(i)=v(i)+dt*f(i)/2
  enddo
else if (switch.eq.2) then
  tempa=0
  do i=1,npart
    v(i)=v(i)+dt*f(i)/2
    tempa=tempa+v(i)^2
  enddo
  tempa=tempa/(s*npart)
  sigma=sqrt(tempa)
  do i=1,npart
    if (rand().lt.nu*dt) then
      v(i)=auss(sima)
    endif
  enddo
endif
return
end

```

1.3 Nosé Thermostat (Tuckerman)

Extended phase space methods can be either Hamiltonian or non-Hamiltonian in their formulation. Here, we begin with a Hamiltonian approach originally introduced by S. Nosé (1983, 1984). Nose's approach can be viewed as a kind of Maxwell daemon. An additional "agent" is introduced into a system that "checks" whether the instantaneous kinetic energy is higher or lower than the desired temperature and then scales the velocities accordingly. Denoting this variable as s and its conjugate momentum as p_s , the Nosé Hamiltonian for a system with physical coordinates $\mathbf{r}_1, \dots, \mathbf{r}_N$ and momenta $\mathbf{p}_1, \dots, \mathbf{p}_N$, takes the

form

$$\mathcal{H}_{Nose'} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2ms^2} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) + \frac{p_s^2}{2Q} + gKT \log(s) \quad (1)$$

where Q is a parameter that determines the time scale on which the daemon acts. Q is not a mass! In fact, it has units of energy \times time². T is the desired temperature of the canonical distribution. If d is the number of spatial dimensions, then the phase space now has a total of $2dN + 2$ dimensions with the addition of s and p_s . The parameter g appearing in Eq. 1 will be determined by the condition that **a micro-canonical distribution of $2dN + 2$ -dimensional phase space of $\mathcal{H}_{Nose'}$ yields a canonical distribution in the $2dN - d$ -dimensional physical phase space**. The presence of s in the kinetic energy is essentially what we would expect for an agent that must scale the kinetic energy in order to control its fluctuations. The choice $gKT \log(s)$ as the potential in s , though seemingly mysterious, is carefully chosen to ensure that a canonical distribution in the physical phase space is obtained. In order to see how the canonical distribution emerges from $\mathcal{H}_{Nose'}$, consider the microcanonical partition function of the full $2dN + 2$ -dimensional phase space:

$$\Omega = \int d\mathbf{r}^N d\mathbf{p}^N ds dp_s \delta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2ms^2} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) + \frac{p_s^2}{2Q} + gKT \log(s) - E \right) \quad (2)$$

where E is the energy of the ensemble. Here we are assuming that there is only one conservation law, the one of the energy. (For clarity, prefactors preceding the integral have been left out.) The distribution of the physical phase space is obtained by integrating over s and p_s . We first introduce a change of momentum variables:

$$\tilde{\mathbf{p}} = \frac{\mathbf{p}}{s}$$

which gives

$$\Omega = \int d\mathbf{r}^N d\tilde{\mathbf{p}}^N s^{3N} ds dp_s \delta \left(\sum_{i=1}^N \frac{\tilde{\mathbf{p}}_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) + \frac{p_s^2}{2Q} + gKT \log(s) - E \right) = \quad (3)$$

(and renaming the dummy variable $\tilde{\mathbf{p}}$ with \mathbf{p})

$$= \int d\mathbf{r}^N d\mathbf{p}^N s^{3N} ds dp_s \delta \left(\mathcal{H} + \frac{p_s^2}{2Q} + gKT \log(s) - E \right) \quad (4)$$

where

$$\mathcal{H} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

is the physical Hamiltonian. We next exploit the properties of the δ -function that

$$\delta(f(s)) = \frac{\delta(s - s_0)}{|f'(s_0)|}$$

where s_0 is the single zero of $f(s)$. (espandendo $f(s)$ intorno al suo zero s_0 abbiamo $f(s) \approx f'(s_0)(s - s_0)$ e quindi occorre fare un cambio di variabile per valutare la delta che porta ad un $f'(s_0)$ a denominatore). The argument of the δ -function in Eq. 4 vanishes when

$$s_0 = e^{\beta(E - \mathcal{H} - \frac{p_s^2}{2Q})/g}$$

so that

$$f'(s) = \frac{gKT}{s} \quad \frac{1}{|f'(s_0)|} = \frac{s_0}{gKT} = \frac{1}{gKT} e^{\beta(E - \mathcal{H} - \frac{p_s^2}{2Q})/g}$$

Substituting in Eq. 4 and integrating over s gives

$$\Omega = \int d\mathbf{r}^N d\mathbf{p}^N e^{3N\beta(E - \mathcal{H} - \frac{p_s^2}{2Q})/g} dp_s \frac{1}{gKT} e^{\beta(E - \mathcal{H} - \frac{p_s^2}{2Q})/g} = \int d^N \mathbf{r} d^N \mathbf{p} e^{(3N+1)\beta(E - \mathcal{H} - \frac{p_s^2}{2Q})/g} dp_s$$

so that, if one choose $g = 3N + 1$ and integrate over p_s one obtains, a part from a pre-factor, the canonical distribution

$$\Omega = \frac{e^{\beta E} \sqrt{2\pi QkT}}{(3N + 1)kT} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta\mathcal{H}}$$

The analysis shows how a microcanonical distribution of the Nosé Hamiltonian $H_{Nose'}$ is equivalent to a canonical distribution in the physical Hamiltonian. This suggests that a molecular dynamics calculation performed using $\mathcal{H}_{Nose'}$ should generate sampling of the canonical distribution $e^{-\beta\mathcal{H}}$ under the usual assumptions of ergodicity. Because the Nosé Hamiltonian mimics the effect of a heat bath by controlling the fluctuations in the kinetic energy, the mechanism of the Nosé Hamiltonian is also known as a thermostating mechanism. The equations of motion generated by $H_{Nose'}$ are

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\partial \mathcal{H}_{Nose'}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{ms^2} & (5) \\ \dot{\mathbf{p}}_i &= -\frac{\partial \mathcal{H}_{Nose'}}{\partial \mathbf{r}_i} = \mathbf{F}_i \\ \dot{s} &= \frac{\partial \mathcal{H}_{Nose'}}{\partial p_s} = \frac{p_s}{Q} \\ \dot{p}_s &= -\frac{\partial \mathcal{H}_{Nose'}}{\partial s} = \sum_i \frac{\mathbf{p}_i^2}{ms^3} - \frac{gKT}{s} = \frac{1}{s} \left[\sum_i \frac{\mathbf{p}_i^2}{ms^2} - gKT \right] \end{aligned}$$

The \mathbf{r}_i and \mathbf{p}_s equations reveal that the thermostating mechanism works on an un-conventional kinetic energy $\sum_i \frac{\mathbf{p}_i^2}{2ms^2}$. This form suggests that the more familiar kinetic energy can be recovered by introducing the following (noncanonical) change of variables:

$$\begin{aligned}
\mathbf{p}'_i &= \frac{\mathbf{p}_i}{s} \\
p'_s &= \frac{p_s}{s} \\
dt' &= \frac{dt}{s}
\end{aligned}
\tag{6}$$

With these new variables, and considering that $d\mathbf{p}_i/dt' = s\mathbf{F}_i$, the evolution is described by

$$\begin{aligned}
\frac{d\mathbf{r}_i}{dt'} &= \frac{\mathbf{p}'_i}{m} \\
\frac{d\mathbf{p}'_i}{dt'} &= \mathbf{F}_i - \frac{sp'_s}{Q}\mathbf{p}'_i \\
\frac{ds}{dt'} &= \frac{s^2p'_s}{Q} \\
\frac{dp'_s}{dt'} &= \frac{1}{s} \left[\sum_i \frac{\mathbf{p}'_i{}^2}{m} - gKT \right] - \frac{s(p'_s)^2}{Q}
\end{aligned}
\tag{7}$$

Because of the noncanonical transformation, these equations lose their symplectic structure, meaning that they are no longer Hamiltonian. In addition, they involve an unconventional definition of time due to the scaling by the variable s . This scaling makes the equations somewhat cumbersome to use directly in the form of Eq. 7.

2 Nose'-Hoover

In 1985, Hoover (1985) introduced a reformulation of the Nose' dynamics that has become one of the staples of molecular dynamics. Starting from the Nose' equations of motion (Eq. [?]), one introduces

a non-canonical change of variables

$$\begin{aligned}\mathbf{p}'_i &= \frac{\mathbf{p}_i}{s} \\ dt' &= \frac{dt}{s} \\ \frac{1}{s} \frac{ds}{dt'} &= \frac{d\eta}{dt'} \\ p_s &= p_\eta\end{aligned}$$

and a redefinition $g = dN$, which leads to new equations of motion of the form

$$\begin{aligned}\frac{d\mathbf{r}_i}{dt'} &= \frac{\mathbf{p}'_i}{m_i} & (8) \\ \frac{d\mathbf{p}'_i}{dt'} &= \mathbf{F}_i - \frac{p_\eta}{Q} \mathbf{p}'_i \\ \frac{d\eta}{dt'} &= \frac{p_\eta}{Q} \\ \frac{dp_\eta}{dt'} &= \sum_{i=1}^N \frac{\mathbf{p}'_i{}^2}{m_i} - dNk_B T\end{aligned}$$

The additional term in the momentum equation acts as a kind of friction term, which, however, can be either negative or positive in sign. In fact, the evolution of the "friction" variable p_η is driven by the difference in the instantaneous value of the kinetic energy (multiplied by 2) and its canonical average $dNk_B T$. Eq. 8 constitute an example of a non-Hamiltonian system. In this case, they are, in a sense, trivially non-Hamiltonian because they are derived from a Hamiltonian system using a noncanonical choice of variables. As we proceed, however, we will encounter examples of systems that are intrinsically non-Hamiltonian, meaning that there is no set of canonical variables that transforms the equations of motion into a Hamiltonian structure.

In order to analyze any non-Hamiltonian system, whether trivial or not, we need to generalize some of the concepts previously developed for non-Hamiltonian phase spaces.

3 Some needed background: Phase space volumes and Liouville's theorem (Tuckerman)

As noted previously, an ensemble is a collection of systems with a set of common macroscopic properties such that each system is in a unique microscopic state at any point in time as determined by its evolution under some dynamical rule, e.g., Hamilton's equations of motion. Given this definition, and assuming that the evolution of the collection of systems is prescribed by Hamilton's equations, it is important first to understand how a collection of microscopic states (which we refer to hereafter simply as "microstates") moves through phase space.

Consider a collection of microstates in a phase space volume element dx_0 centered on the point x_0 . The "0" subscript indicates that each microstate in the volume element serves as an initial condition for Hamilton's equations, which we had written

$$\dot{x} = \eta(x).$$

The equations of motion can be generalized to the case of a set of driven Hamiltonian systems by writing them as $\dot{x} = \eta(x, t)$. We now ask how the entire volume element dx_0 moves under the action of Hamiltonian evolution. Recall that x_0 is a complete set of generalized coordinates and conjugate momenta:

$$x_0 = (q_1(0), q_2(0), \dots, q_{3N}(0), p_1(0) \dots p_{3N}(0))$$

(We will refer to the complete set of generalized coordinates and their conjugate momenta collectively as the phase space coordinates.) If

we follow the evolution of this volume element from $t = 0$ to time t , dx_0 will be transformed into a new volume element dx_t centered on a point x_t in phase space. The point x_t is the phase space point that results from the evolution of x_0 . x_t is a unique function of x_0 that can be expressed as $x(x_0)$. Since the mapping of the point x_0 to x_t is one-to-one, this mapping is equivalent to a coordinate transformation on the phase space from initial phase space coordinates x_0 to phase space coordinates x_t . Under this transformation, the volume element dx_0 transforms according to

$$dx_t = J(x_t; x_0)dx_0 \quad (9)$$

where $J(x_t; x_0)$ is the Jacobian of the transformation, the determinant of the matrix J whose elements are

$$J_{ik} = \frac{\partial x_t^k}{\partial x_0^i}$$

We propose to determine the Jacobian by deriving an equation of motion it obeys and then solving this equation of motion. To accomplish this, we start with the definition,

$$J(x_t; x_0) = \det(J)$$

analyze the derivative

$$\frac{d}{dt}J(x_t; x_0) = \frac{d}{dt}\det(J)$$

and derive a first-order differential equation obeyed by $J(x_t; x_0)$. The time derivative of the determinant is most easily computed by applying an identity satisfied by determinants

$$\det(J) = \exp[\text{Tr}[\ln J]]$$

where Tr is the trace operation:

$$\text{Tr}[J] = \sum_k J_{kk}$$

and $\ln J$ is the matrix that satisfy the identity $e^{\ln J} = J$ (remember that $e^A = 1 + A + A^2/2 + \dots$)

The equivalence between $\det(J)$ and $\exp[\text{Tr}[\ln J]]$ is most easily proved by first transforming J into a representation in which it is diagonal. If J has eigenvalues λ_k , then $\ln(J)$ is a diagonal matrix with eigenvalues $\ln \lambda_k$, and the trace operation yields

$$\text{Tr}[\ln J] = \sum_k \ln \lambda_k.$$

Exponentiating the trace yields $\prod_k \lambda_k$ which is just the determinant of J .

Thus we can write

$$\frac{d}{dt} \det(J) = \frac{d}{dt} e^{\text{Tr}[\ln J]} =$$

deriving respect to t the argument of the exponential

$$= e^{\text{Tr}[\ln J]} \frac{d}{dt} \text{Tr}[\ln J] = e^{\text{Tr}[\ln J]} \text{Tr} \frac{d \ln J}{dt} = e^{\text{Tr}[\ln J]} \text{Tr} \left[\frac{dJ}{dt} J^{-1} \right]$$

where we have used the fact that

$$J = e^{\ln J} = 1 + \ln J + \frac{(\ln J)^2}{2!} + \dots$$

and, element by element

$$\frac{dJ}{dt} = \frac{d \ln J}{dt} + \frac{1}{2!} \frac{d(\ln J)^2}{dt} + \dots = \frac{d \ln J}{dt} + 2 \ln J \frac{1}{2!} \frac{d \ln J}{dt} + \dots$$

which gives

$$= \frac{d \ln J}{dt} [1 + \ln J + \dots] = \frac{d \ln J}{dt} e^{\ln J} = \frac{d \ln J}{dt} J$$

and multiplying by J^{-1} on both sides

$$\frac{d \ln J}{dt} = \frac{dJ}{dt} J^{-1}$$

Note that

$$\frac{dJ_{kl}}{dt} = \frac{\partial \dot{x}_t^k}{\partial x_0^l}$$

and (considering that J^{-1} is simple the reversed in time trajectory)

$$J_{lk}^{-1} = \frac{\partial x_0^l}{\partial x_t^k}$$

Then

$$\frac{d}{dt} J(x_t; x_0) = J(x_t; x_0) \sum_k \sum_l \left[\frac{\partial \dot{x}_t^k}{\partial x_0^l} \frac{\partial x_0^l}{\partial x_t^k} \right]$$

The summation over l of the term in square brackets, is just the chain-rule expression for $\frac{\partial \dot{x}_t^k}{\partial x_t^k}$. Thus, performing this sum yields the equation of motion for the Jacobian:

$$\frac{d}{dt} J(x_t; x_0) = J(x_t; x_0) \sum_k \left[\frac{\partial \dot{x}_t^k}{\partial x_t^k} \right] = J(x_t; x_0) \nabla \cdot x_t \quad (10)$$

where we have made use of the phase space compressibility $\nabla \cdot x_t$. The equation also revealed that the phase compressibility is 0 for a system evolving under Hamilton's equations. Thus, the sum on the right side of eqn. 10 vanishes, and the equation of motion for the Jacobian reduces to

$$\frac{d}{dt} J(x_t; x_0) = 0 \quad (11)$$

This equation of motion implies that the Jacobian is a constant for all time. The initial condition $J(x_0; x_0)$ on the Jacobian is simply 1 since the transformation from x_0 to x_0 is an identity transformation. Thus, since the Jacobian is initially 1 and remains constant in time, it follows that

$$J(x_t; x_0) = 1 \quad (12)$$

Substituting eqn. 12 into eqn.9 yields the volume element transformation condition

$$dx_t = dx_0$$

an important result known as Liouville's theorem (named for the nineteenth-century French mathematician, Joseph Liouville (1809-1882)). Liouville's theorem is essential to the claim made earlier that ensemble averages can be performed at any point in time. If the motion of the system is driven by highly nonlinear forces, then an initial hypercubic volume element dx_0 , for example, will distort due to the chaotic nature of the dynamics. Because of Liouville's theorem, the volume element can spread out in some of the phase space dimensions but must contract in other dimensions by an equal amount so that, overall, the volume is conserved. That is, there can be no net attractors or repellers in the phase space.

4 Classical non-Hamiltonian statistical mechanics - Tuckerman

Generally, Hamiltonian mechanics describe a system in isolation from its surroundings. We have also seen that, with certain tricks, a Hamiltonian system can be used to generate a canonical distribution. But let us examine the problem of a system interacting with its surroundings more closely. If we are willing to treat the system plus surroundings together as an isolated system, then the use of Hamiltonian mechanics to describe the whole is appropriate within a classical description. The distribution of the system alone can be determined by integrating over the variables that represent the surroundings in the microcanonical partition function, as was done above. In most situations, when the surroundings are integrated out in this way, the microscopic equations of motion obeyed by the system are no longer Hamiltonian. In fact, it is often possible to model the effect of the surroundings simply posit-

ing a set of non-Hamiltonian equations of motion and then proving that the equations of motion generate the desired ensemble distribution. Under such a protocol, it is possible to treat systems interacting with heat and particle reservoirs or systems subject to external driving forces. Consequently, it is important to develop an approach that allows us to predict what the phase space distribution function is for a given set of non-Hamiltonian equations of motion. Let us begin by assuming that a system interacting with its surroundings and possibly subject to driving forces is described by non-Hamiltonian microscopic equations of the form

$$\dot{x} = \zeta(x, t)$$

We do not restrict the vector function $\zeta(x, t)$ except to assume that it is smooth and at least once differentiable. In particular, the phase space compressibility $\nabla \cdot \dot{x} = \nabla \cdot \zeta(x, t)$ need not vanish for a non-Hamiltonian system. If it does not vanish, then the system is non-Hamiltonian. Note, however, that the converse is not necessarily true. That is, there are dynamical systems for which the phase space compressibility is zero but which cannot be derived from a Hamiltonian. Recall that the vanishing of the phase space compressibility is central to the derivation of the Liouville theorem and Liouville's equation. Thus, in order to understand how these results change when the dynamics is not Hamiltonian, we need to revisit these derivations.

4.1 The phase space metric

Recall from Section 2.4 that a collection of trajectories initially in a volume element dx_0 about the point x_0 will evolve to dx_t about the point x_t , and the transformation $x_0 \rightarrow x_t$ is a unique one with a Jacobian $J(x_t; x_0)$ satisfying the equation of motion

$$\frac{d}{dt} J(x_t; x_0) = J(x_t; x_0) \nabla \cdot \dot{x}_t \quad (13)$$

Since the compressibility will occur many times in our discussion of non-Hamiltonian systems, we introduce the notation $\kappa(x_t, t)$, to represent this quantity

$$\kappa(x_t, t) = \nabla \cdot x_t$$

Since $\kappa(x_t, t)$ cannot be assumed to be zero, the Jacobian is not unity for all time, and the Liouville theorem $dx_t = dx_0$ no longer holds. The formal solution of Eq, 13, subject to the initial condition $J(x_0; x_0) = 1$ is

$$J(x_t, x_0) = \exp\left[\int_0^t ds \kappa(x_s, s)\right]$$

If we now define a function $w(s)$ such that

$$\kappa(x_s, s) = \frac{d}{ds} w(x_s, s)$$

then

$$J(x_t, x_0) = \exp[w(x_t, t)] \exp[-w(x_0, 0)]$$

Since the phase space volume element evolves according to

$$dx_t = J(x_t; x_0) dx_0$$

we have

$$\begin{aligned} dx_t &= \exp[w(x_t, t)] \exp[-w(x_0, 0)] dx_0 \\ \exp[-w(x_t, t)] dx_t &= \exp[-w(x_0, 0)] dx_0 \end{aligned}$$

which constitutes a generalization of Liouville's theorem; it implies that a weighted phase space volume $\exp[-w(x_t, t)] dx_t$ is conserved rather than simply dx_t . This implies that a conservation law exists on a phase space that does not follow the usual laws of Euclidean geometry. We therefore need to view the phase space of a non-Hamiltonian system in a more general way as a non-Euclidean or Riemannian space or manifold. Riemannian spaces are locally curved spaces and, therefore, it is necessary to consider local coordinates in each neighborhood of

the space. The coordinate transformations needed to move from one neighborhood to another give rise to a nontrivial metric (commonly labeled by \sqrt{g}) and a corresponding volume element denoted

$$\sqrt{g(x_0, 0)} \equiv \exp[-w(x_0, 0)]$$

such that

$$\sqrt{g(x_t, t)}dx_t = \sqrt{g(x_0, 0)}dx_0$$

The implication of the previous equation is that any phase space integral that represents an ensemble average should be performed using $\sqrt{g(x_t, t)}dx$ as the volume element so that the average can be performed at any instant in time.

Imbuing phase space with a metric is not as strange as it might at first seem. After all, phase space is a fictitious mathematical construction, a background space on which a dynamical system evolves. There is no particular reason that we need to attach the same fixed, Euclidean space to every dynamical system. In fact, it is more natural to allow the properties of a given dynamical system dictate the geometry of the phase space on which it lives. Thus, if imbuing a phase space with a metric that is particular to a given dynamical system leads to a volume conservation law, then such a phase space is the most natural choice for that dynamical system. Once the geometry of the phase space is chosen, the form of the Liouville equation and its equilibrium solution are determined, as we will now show.

5 Generalizing the Liouville equation

The important thing to realize is that if the system is not Hamiltonian (for which case $g(x_t, t) = 1$ for all t) the phase space volume need to be multiplied by the function $\sqrt{g(x_t, t)}$ that provides its local curvature

$$\sqrt{g(x_t, t)}dx_t = \sqrt{g(x_0, 0)}dx_0$$

This results in a conservation law of for the probability $f(x_t, t)$ that must incorporate the geometry of space

$$f(x_t, t)\sqrt{g(x_t, t)}dx_t = f(x_0, 0)\sqrt{g(x_0, 0)}dx_0$$

and provides a generalization of the Liouville equation. All averages over phase space must include the $\sqrt{g(x_t, t)}$ term.

For example, the continuity equation that for a space with $g(x_t, t) = 1$ for all t is written as

$$\frac{\partial f(x_t, t)}{\partial t} = -\nabla \cdot f(x_t, t)\dot{x}_t$$

becomes

$$\frac{\partial \sqrt{g(x_t, t)}f(x_t, t)}{\partial t} = -\nabla \cdot \sqrt{g(x_t, t)}f(x_t, t)\dot{x}_t$$

5.1 How to define $f(x)$

In equilibrium, both $f(x_t, t)$ and $g(x_t, t)$ have no explicit time dependence, so that

$$f(x_t)\sqrt{g(x_t)}dx_t = f(x_0)\sqrt{g(x_0)}dx_0 \quad (14)$$

which means that equilibrium averages can be performed at any instant in time, the same as in the Hamiltonian case. To define the function $f(x)$ we follow the same idea encountered in the microcanonical ensemble where the probability of all points with the same energy is assumed to be identical. Here we assume to know all conservation laws satisfied by the constant of motion and associate the same probability to all points in phase space that satisfy all constant of motion and zero probability to all other phase space points.

To be more precise, let there be N_c conservation laws of the form

$$\Lambda_k(x_t) - C_k = 0 \quad \frac{d}{dt}\Lambda_k(x_t) = 0$$

where $k = 1 \dots N_c$. If we can identify these, then a general solution for $f(x)$ can be constructed from these conservation laws in the form

$$f(x) = \prod_{k=1}^{N_c} \delta(\Lambda_k(x_t) - C_k) \quad (15)$$

This solution simply states that the distribution generated by the dynamics is one that samples the intersection of the hypersurfaces represented by all of the conservation laws. Under the usual assumptions of ergodicity, the system will sample all of the points on this intersection surface in an infinite time. Consequently, the non-Hamiltonian system has an associated "microcanonical" partition function obtained by integrating the distribution in Eq. 15:

$$\mathcal{Z} = \int dx \sqrt{g(x)} f(x) = \int dx \sqrt{g(x)} \prod_{k=1}^{N_c} \delta(\Lambda_k(x_t) - C_k)$$

The appearance of the metric determinant in the phase space integral conforms to the requirement of eqn.14, which states that the number of microstates available to the system is determined by $f(x)$ when it is integrated with respect to the conserved volume element $\sqrt{g(x)}dx$. Eqns. 15 lie at the heart of our theory of non-Hamiltonian phase spaces and will be used to analyze a variety of non-Hamiltonian systems in this and subsequent chapters

5.2 Analysis of the Nosé-Hoover equations

We now turn to the analysis of eqns. 8. Our goal is to determine the physical phase space distribution generated by the equations of motion. We begin by identifying the conservation laws associated with the equations. First, there is a conserved energy of the form

$$\mathcal{H}(\mathbf{r}, \eta, \mathbf{p}, p_\eta) = H(\mathbf{r}, \mathbf{p}) + \frac{p_\eta^2}{2Q} + dNkT\eta$$

where $H(\mathbf{r}, \mathbf{p})$ is the physical Hamiltonian. If $\sum_{i=1}^N \mathbf{F}_i \neq 0$ then except for very simple systems, the conservation of the Hamiltonian is the only conservation law. Next, we compute the compressibility. Of all the derivatives (see Eq. 8) the only one which are different from zero are $\nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i$, thus giving

$$\kappa = \sum_{i=1}^N [\nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i] + \frac{\partial \dot{\eta}}{\partial \eta} + \frac{\partial \dot{p}_\eta}{\partial p_\eta} = - \sum_{i=1}^N d \frac{p_\eta}{Q} = -dN\dot{\eta}$$

Since w is the function whose time derivative is κ , we can immediately associate $w = -dN\eta$ and find that the metric is $\sqrt{g} = \exp(-w) = \exp dN\eta$. The microcanonical partition function at a given temperature T can be constructed using \sqrt{g} and the energy conservation condition,

$$\mathcal{Z}(N, V, C_1) = \int d^N \mathbf{p} \int d^N \mathbf{r} \int dp_\eta d\eta \exp [dN\eta] \times \delta(H(\mathbf{r}, \mathbf{p}) + \frac{p_\eta^2}{2Q} + dNkT\eta - C_1)$$

where the T subscript indicates that the microcanonical partition function depends parametrically on the temperature T . The distribution function of the physical phase space can now be obtained by integrating over η and p_η . Using the δ -function to perform the integration over η requires that

$$\eta = \frac{1}{dNkT} \left(C_1 - H(\mathbf{r}, \mathbf{p}) - \frac{p_\eta^2}{2Q} \right)$$

Substitution of this result gives

$$\mathcal{Z}(N, V, C_1) = \frac{e^{\beta C_1}}{dNkT} \int d\mathbf{p}^N \int d\mathbf{r}^N e^{-\beta \mathcal{H}(\mathbf{r}, \mathbf{p})} \int dp_\eta e^{-\beta p_\eta^2 / 2Q}$$

which is the canonical distribution function apart from constant prefactors. This demonstrates that the Nosé-Hoover equations are capable of

generating a canonical distribution in the physical subsystem variables when \mathcal{H} is the only conserved quantity. Unfortunately, this is not the typical situation. In the absence of external forces, Newton's third law requires that $\sum_{i=1}^N \mathbf{F}_i = 0$, which leads to an additional conservation law

$$\mathbf{P}e^\eta = \mathbf{K}$$

where \mathbf{P} is the center-of-mass momentum of the system and \mathbf{K} is an arbitrary constant vector in d dimensions. When this additional conservation law is present, the Nosé-Hoover equations do not generate the correct distribution

6 Nosé-Hoover chains (Tuckerman)

The reason for the failure of the Nosé-Hoover equations when more than one conservation law is obeyed by the system is that the equations of motion do not contain a sufficient number of variables in the extended phase space to offset the restrictions placed on the accessible phase space caused by multiple conservation laws. Each conservation law restricts the accessible phase space by one dimension. In order to counterbalance this effect, more phase space dimensions must be introduced, which can be accomplished by introducing additional variables. But how should these variables be added so as to give the correct distribution in the physical phase space? The answer can be gleaned from the fact that the momentum variable p_η in the Nosé-Hoover equations must have a Maxwell-Boltzmann distribution, just as the physical momenta do. In order to ensure that such a distribution is generated, p_η itself can be coupled to a Nosé-Hoover-type thermostat, which will bring in a new set of variables, η_j and p_{η_j} . But once this is done, we have the problem that p_η must also have a Maxwell-Boltzmann distribution, which requires introducing a thermostat for this variable. We could continue in this way ad infinitum, but the procedure must ter-

minate at some point. If we terminate it after the addition of M new thermostat variable pairs η_j and p_{η_j} , $j = 1 \dots M$, then the equations of motion can be expressed as

$$\begin{aligned}
 \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m} & (16) \\
 \dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{p_{\eta_1}}{Q_1} \mathbf{p}_i \\
 \dot{\eta}_j &= \frac{p_{\eta_j}}{Q_j} \quad j = 1, \dots, M \\
 \dot{p}_{\eta_1} &= \left[\sum_i \frac{\mathbf{p}_i^2}{m} - 3NkT \right] - \frac{p_{\eta_2}}{Q_2} p_{\eta_1} \\
 \dot{p}_{\eta_j} &= \left[\frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \right] - \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \quad j = 2, \dots, M-1 \\
 \dot{p}_{\eta_M} &= \left[\frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT \right]
 \end{aligned}$$

Eqns. 16 are known as the Nosé-Hoover chain equations. These equations ensure that the first $M-1$ thermostat momenta $p_{\eta_1} \dots p_{\eta_{M-1}}$ have the correct Maxwell-Boltzmann distribution. Note that for $M=1$, the equations reduce to the simpler Nosé-Hoover equations. However, unlike the Nosé-Hoover equations, which are essentially Hamiltonian equations in noncanonical variables, the Nosé-Hoover chain equations have no underlying Hamiltonian structure, meaning no canonical variables exist that transform eqns. 16 into a Hamiltonian system. Concerning the parameters Q_1, \dots, Q_M , Martyna et al. (1992) showed that an optimal choice for these is

$$Q_1 = 3NkT\tau^2 \quad Q_j = kT\tau^2 \quad j = 2, \dots, M$$

where τ is a characteristic time scale in the system. Since this time scale might not be known explicitly, in practical molecular dynamics

calculations, a reasonable choice is $\tau > 20\Delta t$ where Δt is the time step.

7 Integrating the Nosé-Hoover chain equations

Numerical integrators for non-Hamiltonian systems such as the Nosé-Hoover chain equations can be derived using the Liouville operator formalism developed previously. However, certain subtleties arise due to the generalized Liouville theorem and, therefore, the subject merits some discussion. Recall that for a Hamiltonian system, any numerical integration algorithm must preserve the symplectic property, in which case, it will also conserve the phase space volume. For non-Hamiltonian systems, there is no clear analog of the symplectic property. Nevertheless, the existence of a generalized Liouville theorem, provides us with a minimal requirement that numerical solvers for non-Hamiltonian systems should satisfy, specifically, the preservation of the measure $\sqrt{g(x)}dx$. Integrators that fail to obey the generalized Liouville theorem cannot be guaranteed to generate correct distributions. Therefore, in devising numerical solvers for non-Hamiltonian systems, care must be taken to ensure that they are measure-preserving (Ezra, 2007).

For an accurate algorithm for the Nose-Hoover chain see Tuckerman's book.

8 The isokinetic ensemble: A simple variant of the canonical ensemble (Tuckerman)

Extended phase space methods are not unique in their ability to generate canonical distributions in molecular dynamics calculations. In this section, we will discuss an alternative approach known as the isokinetic ensemble. As the name implies, the Canonical ensemble isokinetic en-

semble is one in which the total kinetic energy of a system is maintained at a constant value.

Equations of motion for the isokinetic ensemble were first written down by D. J. Evans and G. P. Morriss (1980) by applying Gauss's principle of least constraint. The equations of motion are obtained by imposing a kinetic-energy constraint

$$\sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} = K \quad (17)$$

on the Hamiltonian dynamics of the system. K is twice the kinetic energy. The previous constraint is a nonholonomic constraint (it depends on time), but one that can be expressed in differential form. Thus, the Lagrangian form of the equations of motion is

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = \alpha \sum_i m_i \dot{\mathbf{r}}_i$$

which can also be put into Hamiltonian form

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \alpha \mathbf{p}_i \end{aligned} \quad (18)$$

Here, α is the single Lagrange multiplier needed to impose the constraint. Using Gauss's principle of least constraint gives a closed-form expression for α . We first differentiate eqn.17 once with respect to time, which yields

$$\sum_i \frac{\mathbf{p}_i}{m_i} \cdot \dot{\mathbf{p}}_i = 0$$

Thus, substituting in Eq. 18 gives

$$\sum_i \frac{\mathbf{p}_i}{m_i} \cdot [\mathbf{F}_i - \alpha \mathbf{p}_i] = 0$$

which can be solved for α . Thus, the equations of motion for the isokinetic ensemble become

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{\sum_j \mathbf{p}_j^2 / m_j} \right] \mathbf{p}_i \quad (19)$$

The previous equations are non-Hamiltonian, as we will see by evaluating the phase space compressibility and noticing it is different from zero. In order to carry out the analysis, we first need to calculate the phase space compressibility:

$$\kappa = \sum_{i=1}^N [\nabla_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i] =$$

since $\nabla_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i = 0$ ($\dot{\mathbf{r}}_i$ is \mathbf{p}_i)

$$\sum_{i=1}^N \nabla_{\mathbf{p}_i} \left\{ \mathbf{F}_i - \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{\sum_j \mathbf{p}_j^2 / m_j} \right] \mathbf{p}_i \right\}$$

Since $\nabla_{\mathbf{p}_i} \mathbf{F}_i = 0$, one need only to calculate (indicating with K twice the kinetic energy)

$$\kappa = - \sum_{i=1}^N \nabla_{\mathbf{p}_i} \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} \mathbf{p}_i$$

Evaluating

$$\begin{aligned} \sum_{i=1}^N \nabla_{\mathbf{p}_i} \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} \mathbf{p}_i &= \sum_i \sum_{\alpha} \frac{\partial}{\partial p_{i\alpha}} \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} p_{i\alpha} = \\ & dN \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} + \sum_i \sum_{\alpha} p_{i\alpha} \frac{\partial}{\partial p_{i\alpha}} \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} \\ &= dN \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} + \sum_i \sum_{\alpha} p_{i\alpha} \frac{1}{K^2} \left[K \frac{\partial}{\partial p_{i\alpha}} \sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j - \sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j \frac{\partial K}{\partial p_{i\alpha}} \right] \end{aligned}$$

$$\begin{aligned}
&= dN \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} + \sum_i \sum_\alpha p_{i\alpha} \frac{1}{K^2} \left[K \frac{F_{i,\alpha}}{m_i} - 2 \sum_j \frac{\mathbf{F}_j \cdot \mathbf{p}_j}{m_j} \frac{p_{i\alpha}}{m_i} \right] = \\
&= dN \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} + \frac{1}{K} \sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j - \frac{2}{K^2} \sum_j \frac{\mathbf{F}_j \cdot \mathbf{p}_j}{m_j} \sum_i \sum_\alpha \frac{p_{i\alpha}^2}{m_i} = \\
&= dN \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} + \frac{1}{K} \sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j - \frac{2}{K} \sum_j \frac{\mathbf{F}_j \cdot \mathbf{p}_j}{m_j} = (dN-1) \frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K}
\end{aligned}$$

and substituting

$$\begin{aligned}
\frac{dU}{dt} &= - \sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j \\
\kappa &= \frac{dN-1}{K} \frac{dU(\mathbf{r}_1, \dots, \mathbf{r}_N)}{dt} = \frac{d}{dt} \frac{dN-1}{K} U(\mathbf{r}_1, \dots, \mathbf{r}_N)
\end{aligned}$$

Thus, the function $w(x)$ is just $\frac{dN-1}{K} U(\mathbf{r}_1, \dots, \mathbf{r}_N)$, and the phase space metric becomes

$$\sqrt{g} = e^{-w} = e^{-\frac{dN-1}{K} U(\mathbf{r}_1, \dots, \mathbf{r}_N)}$$

Since the equations of motion explicitly conserve the total kinetic energy we can immediately write down the partition function generated by the equation of motion

$$\Omega = \int d\mathbf{p}^N d\mathbf{r}^N e^{-\frac{dN-1}{K} U(\mathbf{r}_1, \dots, \mathbf{r}_N)} \delta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} - (dN-1)k_B T \right)$$

The analysis shows that if the constant parameter K (the kinetic energy) is chosen to be $(dN-1)k_B T$, then the partition function becomes

$$\Omega = \int d\mathbf{p}^N d\mathbf{r}^N \mathbf{r} e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} \delta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} - (dN-1)k_B T \right)$$

which is the partition function of the isokinetic ensemble. Indeed, the constraint condition $\delta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} - (dN - 1)k_B T \right)$ is exactly what we would expect for a system with a single kinetic-energy constraint based on the virial theorem, since the number of degrees of freedom is $dN - 1$ rather than dN .

8.1 Numerical Integrator

A simple yet effective integrator for the isokinetic equations can be obtained by applying the Liouville operator approach. As usual, we begin by writing the total Liouville operator

$$iL = \sum_{i=1}^N \left[\frac{\mathbf{p}_i}{m_i} \cdot \nabla_{\mathbf{r}_i} + \left(\mathbf{F}_i - \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} \right] \mathbf{p}_i \right) \cdot \nabla_{\mathbf{p}_i} \right]$$

as the sum of two contributions $iL = iL_1 + iL_2$ where

$$iL_1 = \sum_{i=1}^N \frac{\mathbf{p}_i}{m_i} \cdot \nabla_{\mathbf{r}_i}$$

and

$$iL_2 = \sum_{i=1}^N \left(\mathbf{F}_i - \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{K} \right] \mathbf{p}_i \right) \cdot \nabla_{\mathbf{p}_i}$$

The approximate evolution of an isokinetic system over a time Δt is obtained by acting with a Trotter factorized operator $\exp(iL\Delta t) = \exp(iL_2\Delta t/2)\exp(iL_1\Delta t)\exp(iL_2\Delta t/2)$ on an initial condition $\mathbf{p}(0), \mathbf{r}(0)$. The action of each of the operators in this factorization can be evaluated analytically (Zhang, 1997; Minary et al., 2003).

The action of $\exp(iL_2\Delta t/2)$ refer to the evolution of the momenta. Hence it propagate \mathbf{p} . But we can use Eq. 19 to solve analytically the evolution of \mathbf{p} for $\Delta t/2$ by solving the coupled first-order differential

equations (but in the same spirit of the propagation, with \mathbf{r}^N and $\mathbf{F}(\mathbf{r})^N$ held fixed at the value at time t). In this way, the momentum propagation is given by (Eq. 19)

$$\frac{dp_{i,\alpha}}{dt} = F_{i,\alpha} - \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{2K} \right] p_{i,\alpha} = F_{i,\alpha} - \dot{h}(t)p_{i,\alpha}$$

with $\mathbf{r}_1, \dots, \mathbf{r}_N$ (and hence $F_{i,\alpha}$) held fixed. Here, we explicitly index both the spatial components ($\alpha = 1, \dots, d$) and particle numbers $i = 1, \dots, N$.

If we define a function

$$y(t) = \frac{y(0) + a \int_0^t e^{h(t')} dt'}{e^{h(t)}}$$

its time derivative is

$$\dot{y} = \frac{ae^{h(t)}e^{h(t)} - [y(0) + a \int_0^t e^{h(t')} dt']e^{h(t)}\dot{h}}{(e^{h(t)})^2} = a - y(t)\dot{h}(t)$$

Hence the solution can be written as

$$p_{i,\alpha}(t) = \frac{p_{i,\alpha}(0) + F_{i,\alpha} \int_0^t e^{h(t')} dt'}{e^{h(t)}}$$

and by defining

$$\dot{s}(t) = e^{h(t)}$$

or

$$\begin{aligned} s(t) &= \int_0^t e^{h(t')} dt' \\ p_{i,\alpha}(t) &= \frac{p_{i,\alpha}(0) + F_{i,\alpha} s(t)}{\dot{s}(t)} \end{aligned} \tag{20}$$

Deriving the definition of $\dot{s}(t)$ one get

$$\ddot{s}(t) = \frac{d}{dt}e^{h(t)} = \dot{h}(t)\dot{s}(t)$$

or

$$\ddot{s}(t) = \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j / m_j}{2K} \right] \dot{s}(t) = \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j \dot{s}(t) / m_j}{2K} \right]$$

But since (eq. 20) $\mathbf{p}_i \dot{s}(t) = \mathbf{p}_i(0) + \mathbf{F}_i s(t)$

$$\ddot{s}(t) = \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_i(0) / m_j}{2K} \right] + \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{F}_j / m_j}{2K} \right] s(t)$$

As know, the Eq. $\ddot{s} = a + bs$ has as a solution

$$s(t) = \frac{a}{b} \left(\cosh(t\sqrt{b}) - 1 \right) + \frac{1}{\sqrt{b}} \sinh(t\sqrt{b}) \quad (21)$$

where

$$a = \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{p}_j(0) / m_j}{2K} \right] \quad (22)$$

and

$$b = \left[\frac{\sum_j \mathbf{F}_j \cdot \mathbf{F}_j / m_j}{2K} \right]$$

Similarly, one can calculate exactly $\dot{s}(t)$.

The operator is applied by simply evaluating eqn. 21 and its derivative at $t = \Delta t/2$. The action of the operator $\exp(iL_1 \Delta t)$ on a state (\mathbf{p}, \mathbf{r}) yields

$$\begin{aligned} \exp(iL_1 \Delta t) \mathbf{p}_i &= \mathbf{p}_i \\ \exp(iL_1 \Delta t) \mathbf{r}_i &= \mathbf{r}_i + \Delta t \mathbf{p}_i, \end{aligned}$$

which has no effect on the momenta.

The combined action of the three operators in the Trotter factorization leads to the following reversible, kinetic energy conserving algorithm for integrating the isokinetic equations:

- 1. Evaluate new $s(\Delta t/2), \dot{s}(\Delta t/2)$ and update the momenta according to

$$\mathbf{p}_i \leftarrow \frac{\mathbf{p}_i + \mathbf{F}_i s(\Delta t/2)}{\dot{s}(\Delta t/2)}$$

- 2. Using the new momenta, update the positions according to

$$\mathbf{r}_i \leftarrow \mathbf{r}_i + \Delta t \mathbf{p}_i$$

- 3. Calculate new forces using the new positions.
- 4. Evaluate new $s(\Delta t/2), \dot{s}(\Delta t/2)$ and update the momenta according to

$$\mathbf{p}_i \leftarrow \frac{\mathbf{p}_i + \mathbf{F}_i s(\Delta t/2)}{\dot{s}(\Delta t/2)}$$

Note, $s(\Delta t/2), \dot{s}(\Delta t/2)$ are evaluated by substituting the present momentum and the forces into eqns. 22 with $t = \Delta t/2$. The symbol, \leftarrow indicates that on the computer, the values on the left-hand side are overwritten in memory by the values on the right-hand side. The isokinetic ensemble method has recently been shown to be a useful method for generating a canonical coordinate distribution. First, it is a remarkably stable method, allowing very long time steps to be used, particularly when combined with the RESPA scheme. Unfortunately, the isokinetic approach suffers from some of the pathologies of the Nosé-Hoover approach so some care is needed when applying it. Minary et al. (2004b) showed that such problems can be circumvented by combining the isokinetic and Nosé-Hoover chain approaches.

9 Molecular Dynamics at constant pressure - Frenkel-Smith

Most experiments are performed at constant pressure instead of constant volume. If one is interested in simulating the effect of, for example, the composition of the solvent on the properties of a system one has to adjust the volume of an N,V,T simulation to ensure that the pressure remains constant. For such a system it is therefore much more convenient to simulate at constant pressure. To simulate at constant pressure in a Molecular Dynamics simulation the volume is considered

as a dynamical variable that changes during the simulation. In Chapter 5 we have seen that one can perform Monte Carlo simulations at constant pressure by changing the volume of the simulation box. Here we consider the equivalent for a Molecular Dynamics simulation. Similar to the Monte Carlo case, this is an excellent method for homogeneous fluids. For inhomogeneous systems, however, one may need to change the shape of the simulation box as well [102,103]. In Appendix B we have shown that the correct thermostating of a Molecular Dynamics simulation has many subtleties related to the conservation laws and whether a simulation is performed with a fixed center of mass. Similar problems arise with the isothermal-isobaric ensemble. The earlier scheme of Hoover [132] can only approximate the desired distribution [137]. Since the scheme of Martyna et al. does give the desired distribution, we focus on this scheme. All these schemes are based on the extended ensemble approach pioneered by Andersen [104]. The equations of motion proposed by Martyna et al. [138] for the positions and the momenta are

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W} \mathbf{r}_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \left(1 + \frac{1}{N}\right) \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_{\xi_1}}{Q_1} \mathbf{p}_i\end{aligned}$$

where N is the number of particles. In these equations of motion we recognize a thermostat that is introduced via the variables ξ_1 , p_{ξ_1} and Q_1 similar to the N, V, T version of the Nosé-Hoover chain algorithm. A barostat is introduced via the variables ϵ , p_ϵ and W . ϵ is defined as the logarithm of the volume V of the system

$$\epsilon = \ln \frac{V}{V(0)}$$

where $V(0)$ is the volume at $t = 0$, W is the mass parameter associated to ϵ and p_ϵ is the momentum conjugate to ϵ . The equations of

motion are complemented with an equation of motion for the volume, which reads in d dimensions

$$\dot{V} = \frac{dV p_\epsilon}{W}$$

$$\dot{p}_\epsilon = dV(P_{int} - P_{ext}) + \frac{1}{N} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - \frac{p_{\epsilon_1}}{Q_1} p_\epsilon$$

In these equations P_{ext} is the external pressure, which is imposed (like the temperature). P_{int} is the internal pressure, which can be calculated during the simulation

$$P_{INT} = \frac{1}{dV} \left[\sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{m_i} + \mathbf{r}_i \cdot \dot{\mathbf{F}}_i \right) - dV \frac{\partial U(V)}{\partial V} \right]$$

where U is the potential. This equation differs from the conventional virial equation for a constant-volume simulation. The equations of the chain of length M are

$$\dot{\xi}_k = \frac{p_{\xi_k}}{Q_k} \quad k = 1, M$$

$$\dot{p}_{\xi_1} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (dN + 1)k_B T - \frac{p_{\xi_2}}{Q_2} p_{xi_2}$$

$$\dot{p}_{\xi_k} = \frac{p_{\xi_{k-1}}^2}{Q_{k-1}} - k_B T - \frac{p_{\xi_{k+1}}^2 Q_{k+1} p_{\xi_k}}{Q_{k+1}} \quad k = 2 \dots M - 1$$

$$\dot{p}_{\xi_M} = \frac{p_{\xi_{M-1}}^2}{Q_{M-1}} - k_B T$$